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(57) Abstract

The present invention provides a needled mat for reinforcing a composite, composites formed therefrom, and methods related thereto. The needled mat includes (a) a non–woven primary layer having a sublayer of glass fiber strands oriented generally perpendicularly to the longitudinal axis of the mat positioned between sublayers of glass fiber strands oriented generally parallel to a longitudinal axis of the mat; and (b) a secondary layer of randomly oriented continuous and/or chopped glass fiber strands.

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GLASS FIBER MATS, COMPOSITES REINFORCED WITH THE SAME AND METHODS FOR MAKING THE SAME

Field of the Invention

This invention relates generally to glass fiber mats, composites reinforced with the same and methods for making the same. More particularly, this invention relates to needled mats having (a) a non-woven primary layer having a sublayer of glass fiber strands oriented generally perpendicularly to the longitudinal axis of the mat positioned between sublayers of glass fiber strands oriented generally parallel to a longitudinal axis of the mat; and (b) a secondary layer of randomly oriented continuous and/or chopped glass fiber strands.

Background of the Invention

Composites of reinforcements and thermoplastic or thermosetting matrix materials can be formed by various molding techniques such as compression molding or stamping (thermoplastic operations) and pultrusion, filament winding, vacuum molding, compression or injection molding and open lay-up molding (thermoset operations). The resulting composites can be used in such applications as automobile components, boat hulls, fishing rods and housings for computers.

The configuration and type of reinforcement have a pronounced effect on the physical characteristics of the composite, such as density, compressive strength and shear strength. Preferred reinforcement configurations often vary greatly for different molding processes and molding conditions.

The matrix material selected can also influence the selection of reinforcement type and configuration. In thermosetting molding operations, good "wet-through" (penetration of the polymeric matrix material through the mat) and "wet-out" (penetration of the polymeric matrix material through the

individual bundles or strands of fibers in the mat) properties are desirable. In contrast, good dispersion properties are of predominant concern in typical thermoplastic molding operations.

For reinforcing plastic articles, U.S. Patent No. 3,614,936 discloses a nonwoven structure of chopped glass strand which is stitched together. Optionally, the nonwoven structure can include parallel glass strands lengthwise of the structure (see col. 6, lines 48-55). The stitched nonwoven structure can be compacted with heated rollers to fuse the stitching thread and then needled (see col. 4, lines 14-30).

U.S. Patent No. 4,749,613 discloses a thermoplastic stampable sheet composed of 30 to 80 percent by weight of reinforcing fibers arranged in one direction needled together with a swirled continuous strand mat, the sheet being impregnated with a thermoplastic resin.

U.S. Patent No. 4,931,358 discloses a material consisting of a thermoplastic polymer and a needled textile fabric consisting of at least two layers of continuous filament yarn oriented in at least one preferred direction and at least one layer of unoriented fibers.

U.S. Patents Nos. 5,540,986 and 5,129,131 disclose a stampable sheet of thermoplastic resin reinforced with a glass fiber mat having a layer of non-oriented fibers and a layer of unidirectional fibers which are mechanically intertwined.

None of the foregoing references address the problems encountered in molding thermosetting composites, such as wet-out and compatibility between the reinforcement and the thermosetting matrix material.

U.S. Patent No. 4,278,720 discloses a mat useful in thermosetting sheet molding compounding which has two layers of parallel strand oriented at a 45 degree angle to the longitudinal axis of the mat and a layer of randomly oriented strand positioned therebetween, the points of intersection of the strands being bonded by an organic binder, as discussed at column 2,

lines 26-35. Use of organic binders in mat formation is not desirable for environmental reasons.

There is a long-felt need in the polymeric molding industry to provide a glass fiber reinforcement which is compatible with and can be readily impregnated by both thermoplastic or thermosetting matrix materials, which can be used in a wide variety of molding applications to provide good uniformity of glass distribution, flow into complex mold shapes and handling characteristics and which provides a composite having good surface smoothness and mechanical properties such as flexibility, strength and high density.

Summary of the Invention

One aspect of the present invention is a mat adapted to reinforce a polymeric matrix material, the mat comprising: (a) a non-woven primary layer comprising (i) a first sublayer of a plurality of generally parallel, essentially continuous glass fiber strands oriented generally parallel to a longitudinal axis of the mat; (ii) a second sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the first sublayer and being oriented generally perpendicularly to the longitudinal axis of the mat; (iii) a third sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat; and (b) a secondary layer positioned adjacent to a surface of the primary layer, the secondary layer comprising a plurality of randomly oriented, generally continuous glass fiber strands, wherein the strands of the primary layer are entangled with the strands of the secondary layer by needling together at least a portion of the strands of the primary layer and the strands of the secondary layer to form a mat.

Another aspect of the present invention is a mat adapted to reinforce a polymeric matrix material, the mat comprising: (a) a non-woven primary layer comprising (i) a first sublayer of a plurality of generally parallel, essentially continuous glass fiber strands oriented generally parallel to a longitudinal axis of the mat; (ii) a second sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the first sublayer and being oriented generally perpendicularly to the longitudinal axis of the mat; (iii) a third sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat; and (b) a secondary layer positioned adjacent to a surface of the primary layer, the secondary layer comprising a plurality of randomly oriented glass fibers having a mean average length ranging from about 25 to about 100 millimeters, wherein the strands of the primary layer are entangled with the strands of the secondary layer by needling together at least a portion of the strands of the primary layer and the fibers of the secondary layer to form a mat.

Another aspect of the present invention is a reinforced polymeric composite comprising: (a) a polymeric matrix material; and (b) a reinforcing mat comprising: (1) a non-woven primary layer comprising (i) a first sublayer of a plurality of generally parallel, essentially continuous glass fiber strands oriented generally parallel to a longitudinal axis of the mat; (ii) a second sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the first sublayer and being oriented generally perpendicularly to the longitudinal axis of the mat; (iii) a third sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat; and (2) a secondary layer positioned adjacent to a surface of the primary layer, the secondary layer

comprising a plurality of randomly oriented, generally continuous glass fiber strands, wherein the strands of the primary layer are entangled with the strands of the secondary layer by needling together at least a portion of the strands of the primary layer and the strands of the secondary layer to form a mat for reinforcing the polymeric matrix material.

Another aspect of the present invention is a method for making a mat adapted to reinforce a polymeric matrix material, the method comprising the steps of: (a) positioning a plurality of generally parallel, essentially continuous glass fiber strands generally parallel to a longitudinal axis of the mat to form a first sublayer of a primary layer; (b) positioning a plurality of generally parallel, essentially continuous glass fiber strands upon a surface of the first sublayer and being oriented generally perpendicularly to the longitudinal axis of the mat to form a second sublayer of the primary layer; (c) positioning a plurality of generally parallel, essentially continuous glass fiber strands upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat to form a third sublayer of the primary layer; (d) dispersing a plurality of essentially continuous glass fiber strands upon a surface of the primary layer to form a secondary layer, such that the glass fiber strands of the secondary layer are randomly oriented; and (e) entangling the glass fiber strands of the primary layer with the glass fiber strands of the secondary layer by needling at least a portion of the strands of the primary layer and the strands of the secondary layer together to form a mat.

Another aspect of the present invention is a method for reinforcing a polymeric matrix material to form a reinforced composite, the method comprising the steps of: (a) positioning a plurality of generally parallel, essentially continuous glass fiber strands generally parallel to a longitudinal axis of the mat to form a first sublayer of a primary layer; (b) positioning a plurality of generally parallel, essentially continuous glass fiber strands upon a surface of the first sublayer and being oriented generally perpendicularly to

the longitudinal axis of the mat to form a second sublayer of the primary layer; (c) positioning a plurality of generally parallel, essentially continuous glass fiber strands upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat to form a third sublayer of the primary layer; (b) dispersing a plurality of essentially continuous glass fiber strands upon a surface of the primary layer to form a secondary layer, such that the glass fiber strands of the secondary layer are randomly oriented; (c) entangling the glass fiber strands of the primary layer with the glass fiber strands of the secondary layer by needling at least a portion of the strands of the primary layer and the strands of the secondary layer together to form a mat; (d) coating and impregnating at least a portion of the mat with the polymeric matrix material; and (e) at least partially curing the polymeric matrix material to form a reinforced composite.

Brief Description of the Drawings

The foregoing summary, as well as the following detailed description of the preferred embodiments, will be better understood when read in conjunction with the appended drawings. In the drawings:

Fig. 1 is an enlarged schematic perspective view of a portion of a mat, according to the present invention;

Fig. 2 is a cross sectional view of the mat of Fig. 1, taken along lines 2-2 of Fig. 1;

Fig. 3 is an enlarged end view of a portion of an alternative embodiment of a mat, according to the present invention;

Fig. 4 is an enlarged end view of a portion of another alternative embodiment of a mat, according to the present invention;

Fig. 5 is an enlarged end view of a portion of another alternative embodiment of a mat, according to the present invention;

Fig. 6 is an enlarged schematic perspective view of a portion of another alternative embodiment of a mat, according to the present invention;

Fig. 7 is an enlarged end view of a portion of another alternative embodiment of a mat, according to the present invention; and

Fig. 8 is a schematic perspective view of a system for forming a mat according to the present invention; and

Fig. 9 is an enlarged schematic cross sectional view of a composite, according to the present invention.

Detailed Description of the Preferred Embodiments

The mats of the present invention are useful for reinforcing thermosetting matrix materials to form composites for such applications as boat hulls, light poles, utility poles and support pilings. During fabrication of the composite, the mats of the present invention exhibit good structural integrity which facilitates handling of the mat and enables the fabricator to decrease mold cycle times. The mats of the present invention can be used as a single ply to reduce cost and decrease fabrication time, yet conform to a wide variety of intricate mold shapes in challenging molding operations, such as vacuum molding.

The mat of the present invention also provide numerous advantages in thermoplastic composite molding processes such as GMT, including but not limited to good permeability for impregnation by the thermoplastic matrix material, good uniformity of glass distribution and flow into complex mold shapes and provides composites having good surface smoothness and mechanical properties, such as tensile, flexural and compressive strength, tensile and flexural modulus and stiffness.

Thermoset composites fabricated from the mats of the present invention exhibit good flexibility and high density to provide good load bearing

capabilities, as well as high shear strength, compressive strength and interlaminar shear strength.

Referring to the drawings, wherein like numerals indicate like elements throughout, there is shown in Figs. 1 and 2 a preferred embodiment of a mat, generally designated 10, in accordance with the present invention. The mat 10 comprises one or more non-woven primary, support layers 12 and one or more secondary layers 14 positioned adjacent to a surface 16 of the primary layer 12.

As shown in Fig. 1, the preferred mat 10 has a single primary layer 12 and a single secondary layer 14. In an alternative embodiment shown in Fig. 3, the mat 310 can have a plurality of primary layers 312 and/or a plurality of secondary layers 314. For example, one or more secondary layers 314 can be positioned adjacent to the upper surface 316 and/or the lower surface 317 of the primary layer 312, as desired. In another alternative embodiment shown in Fig. 5, the mat 510 has a single primary layer 512 and a plurality of secondary layers 514.

The primary layer 12 generally comprises about 20 to about 90 weight percent of the mat 10, preferably about 50 to about 80 weight percent, and more preferably about 60 to about 80 weight percent of the mat on a total solids basis.

Referring now to Fig. 1, the primary layer 12 comprises one or more first sublayers 17, one or more second sublayers 19 positioned adjacent to a surface 21 of the first sublayer, and one or more third sublayers 23 positioned adjacent to a surface 25 of the second sublayer 19. As used herein, "non-woven" means that the first, second and third sublayers 17, 19, 23 are present as individual layers and are not interwoven by a process such as knitting or weaving. Portions of the first, second and third sublayers 17, 19, 23 are, however, intermingled by the needling process to which the overall mat is subjected during processing. Forming the sublayers 17, 19, 23 as

individual layers provides unique processing and cost advantages which will be discussed in detail below.

As shown in Fig. 1, the first sublayer 17 comprises a plurality of unidirectional, generally parallel essentially continuous strands 18 of glass fibers 20. As used herein, the term "fibers" means a plurality of individual filaments. The terms "strand" or "bundle" as used herein refer to a plurality of fibers.

As used herein, the phrase "essentially continuous" means that the glass fiber strands 18 can have a mean average length of about 10 meters to about 400 kilometers (km), and preferably have a mean average length of about 500 to about 1500 meters.

The phrase "unidirectional" means that the glass fiber strands 18 of the first sublayer 17 are oriented generally parallel to a longitudinal axis 22 of the mat 10 (shown in Fig. 1). The phrase "generally parallel to a longitudinal axis 22 of the mat" means that the glass fiber strands 18 are oriented at an angle of less than about 25 degrees with respect to the longitudinal axis 22 of the mat 10. Preferably the glass fiber strands 18 are oriented at an angle of less than about 10 degrees with respect to the longitudinal axis 22 of the mat 10 and, more preferably, the glass fiber strands 18 are parallel to the longitudinal axis 22 of the mat 10, as shown in Fig. 1.

Orienting the glass fiber strands 18 of the first sublayer 17 of the mat 10 generally parallel to the longitudinal axis 22 of the mat 10 provides good mechanical strength in the direction of the strand orientation to a composite reinforced with the mat, which is advantageous for support structures such as columns, pilings and poles in which highly directionalized strength and stiffness is desired.

Referring now to Fig. 2, the average distance 24 between the outer surface 26 of a first glass fiber strand 28 and the nearest outer surface 30 of a second, adjacent glass fiber strand 32 can range from about 0.1 to about 20

millimeters (mm), and is preferably about 0.1 to about 10 mm and more preferably about 0.1 to about 5 mm. One skilled in the art would understand that the distance 24 or spacing between pairs of strands can be the same or different for different pairs of strands, as desired. The number of strands (ends) per centimeter of width 40 of the primary layer 12 ranges from about 0.5 to about 500 ends per centimeter, and is preferably about 1 to about 10.

The first sublayer 17, 313 can be a monolayer (shown in Fig. 1) or can comprise multiple layers 319, 321 (shown in Fig. 3) of strands 323, 325 which can be layered such that the respective central longitudinal axes 327, 329 of the strands 323, 325 are vertically aligned or offset, as desired.

The first sublayer 17 generally comprises about 10 to about 50 weight percent of the mat 10.

Referring to Fig. 1, the second sublayer 19 is positioned adjacent to, and preferably in facing engagement with, the surface 21 of the first sublayer 17. The second sublayer 19 comprises a plurality of generally parallel essentially continuous strands 27 of glass fibers 29 which are oriented generally perpendicularly to the longitudinal axis 22 of the mat 10 (shown in Fig. 1). The phrase "generally perpendicular(ly) to the longitudinal axis 22 of the mat" means that the glass fiber strands 27 are oriented at an angle 69 ranging from about 70 degrees to about 110 degrees with respect to the longitudinal axis 22 of the mat 10. Preferably the glass fiber strands 27 are oriented at an angle ranging from about 85 degrees to about 95 degrees with respect to the longitudinal axis 22 of the mat 10 and, more preferably, the glass fiber strands 27 are perpendicular (oriented 90 degrees) to the longitudinal axis 22 of the mat 10, as shown in Fig. 1.

Orienting the glass fiber strands 27 of the second sublayer 19 of the mat 10 generally perpendicular to the longitudinal axis 22 of the mat 10 provides good mechanical cross-strength to a composite reinforced with the

mat, which is advantageous for applications in which good cross-strength is also desired.

Referring now to Fig. 1, the average distance 31 between the outer surface 33 of a first glass fiber strand 35 and the nearest outer surface 37 of a second, adjacent glass fiber strand 39 of the second sublayer can range from about 0.1 to about 20 millimeters (mm), and is preferably about 0.1 to about 10 mm and more preferably about 0.1 to about 5 mm. One skilled in the art would understand that the distance 31 or spacing between pairs of strands can be the same or different for different pairs of strands, as desired. The number of ends per centimeter of length of the second sublayer 19 ranges from about 0.5 to about 500, and is preferably about 1 to about 10.

The second sublayer 19, 315 can be a monolayer (shown in Fig. 1) or can comprise multiple layers 335, 337 (shown in Fig. 3) of strands 339, 341 which can be layered such that the respective central longitudinal axes 357, 359 of the strands 339, 341 are vertically aligned or offset, as desired.

The second sublayer 19 generally comprises about 10 to about 50 weight percent of the mat 10.

Referring to Fig. 1, the third sublayer 23 is positioned adjacent to, and preferably in facing engagement with, the surface 25 of the second sublayer 19. The third sublayer 23 comprises a plurality of unidirectional, generally parallel, essentially continuous strands 43 of glass fibers 45. The configuration of the third sublayer 23 is similar to the configuration of the first sublayer 17, which is discussed in detail above. The third sublayer 23, 343 can be a monolayer (shown in Fig. 1) or can comprise multiple layers 345, 347 (shown in Fig. 3) of strands 349, 351 which can be layered such that the respective central longitudinal axes 353, 355 of the strands 349, 351 are vertically aligned or offset, as desired. The third sublayer 23 generally comprises about 10 to about 50 weight percent of the mat 10.

The first sublayer 17, second sublayer 19 and third sublayer 23 of the primary layer 12 of the mat 10 comprise glass fibers 20, 29, 45, a class of fibers generally accepted to be based upon oxide compositions such as silicates selectively modified with other oxide and non-oxide compositions. Useful glass fibers can be formed from any type of fiberizable glass composition known to those skilled in the art, and include those prepared from fiberizable glass compositions such as "E-glass", "A-glass", "C-glass", "D-glass", "R-glass", "S-glass", and E-glass derivatives that are fluorine-free and/or boron-free. Preferred glass fibers are formed from E-glass. Such compositions and methods of making glass filaments therefrom are well known to those skilled in the art and further discussion thereof is not believed to be necessary in view of the present disclosure. If additional information is needed, such glass compositions and fiberization methods are disclosed in K. Loewenstein, The Manufacturing Technology of Continuous Glass Fibres, (3d Ed. 1993) at pages 30-44, 47-60, 115-122 and 126-135, which are hereby incorporated by reference.

The glass fibers 20 can have a nominal filament diameter ranging from about 5.0 to about 35.0 micrometers (corresponding to a filament designation of D through U and above), and preferably have a nominal filament diameter ranging from about 9.0 to about 30.0 micrometers. For further information regarding nominal filament diameters and designations of glass fibers, see Loewenstein at page 25, which is hereby incorporated by reference.

Referring to Figs. 1 and 2, the number of fibers per strand 18, 27, 43, can range from about 100 to about 15,000, and is preferably about 200 to about 7000. For more information regarding glass fiber strand designations, see Loewenstein at page 27, which is hereby incorporated by reference.

Referring now to Fig. 1, the glass fibers 20, 29, 45 are coated on at least a portion of their outer surfaces 36, 51, 53 with a layer 38, 55, 57 comprising a first coating composition which is compatible with the polymeric

thermoplastic or thermosetting matrix material, i.e., the components of the first coating composition facilitate wet-out and wet-through of the matrix material upon the fiber strands 18, 27, 43 and provide adequate physical properties in the composite.

Suitable first coating compositions include sizing compositions and/or secondary coating compositions. As used herein, the terms "size", "sized" or "sizing" refer to the aqueous composition applied to the filaments immediately after formation of the glass fibers. The term "secondary coating" refers to a coating composition applied secondarily to one or a plurality of strands after the sizing composition is applied, and preferably at least partially dried.

In a preferred embodiment, the first coating composition comprises one or more polymeric film forming materials which are compatible with a thermosetting matrix material. As used herein, the phrase "compatible with the thermosetting matrix material" means that the components of the first coating composition facilitate wet-through and wet-out of the matrix material upon the fiber strands 18, provide adequate physical properties in the composite, are chemically compatible with the thermosetting matrix material and are resistant to hydrolysis. The measure of the penetration of the polymeric matrix material through the mat is referred to as "wet-through". The measure of the flowability of the polymeric matrix material through the glass fiber mass to obtain essentially complete encapsulation of the entire surface of each glass fiber by the polymeric matrix material is referred to as "wet-out".

Suitable polymeric film forming materials which are compatible with a thermosetting matrix material include one or more thermosetting materials, one or more vinyl acetate materials, one or more thermoplastic polyester materials, and mixtures thereof.

Examples of suitable thermosetting film-forming materials include aminoplasts, alkyds, phenolics, polyepoxides, thermosetting polyesters, thermosetting polyurethanes, derivatives, copolymers and mixtures thereof.

Useful aminoplasts include urea-formaldehydes and melamine formaldehydes such as RESIMENE 841 which is commercially available from Monsanto Co. of St. Louis, Missouri. A non-limiting example of a phenolic suitable for use in the present invention is phenol formaldehyde.

Useful polyepoxides contain at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols. Useful polyglycidyl ethers of polyhydric alcohols can be formed by reacting epihalohydrins and/or butadiene dioxide with polyhydric alcohols, such as dihydric alcohols, in the presence of an alkali condensation and dehydrohalogenation catalyst such as sodium hydroxide or potassium hydroxide. An example of a suitable commercially available epoxy film-forming polymer is EPON® 880 epoxy resin, which is an epoxy functional polyglycidyl ether of bisphenol A prepared from bisphenol-A and epichlorohydrin and is commercially available from Shell Chemical Company of Houston, Texas.

Suitable thermosetting polyurethanes include BAYBOND XW-110, which is commercially available from Bayer Corp. of Pittsburgh, Pennsylvania and other thermosetting polyurethanes which are commercially available from Bayer and E.I. duPont de Nemours Co. of Wilmington, Delaware.

A preferred thermosetting polyester material is RD-847A polyester resin which is commercially available from Borden Chemicals of Columbus, Ohio. Other suitable thermosetting polyesters are STYPOL polyesters which are commercially available from Cook Composites and Polymers of Port Washington, Wisconsin and thermosetting NEOXIL polyesters which are commercially available from DSM B.V. of Como, Italy.

As discussed above, thermoplastic vinyl acetate materials and thermoplastic polyester materials which are compatible with the thermosetting matrix material can also be used as polymeric film-forming materials in the present invention. Non-limiting examples of useful thermoplastic vinyl acetate

polymers include RESYN 1971, RESYN 2828 and RESYN 1037 vinyl acetate copolymer emulsions which are commercially available from National Starch, VINOL polyvinyl acetates which are commercially available from Air Products and Chemicals Co. of Allentown, Pennsylvania and other polyvinyl acetates which are commercially available from H. B. Fuller.

Thermoplastic polyesters useful in the present invention include saturated bisphenol A polyesters such as Neoxil 954D which is commercially available from DSM, B.V. of the Netherlands.

Preferably the first coating composition comprises a polyepoxide such as EPON® 880 and a thermosetting polyester material such as RD-847A polyester resin in a ratio of about 1:1 to about 6:1 on a total weight basis.

In an alternative embodiment, the first coating composition is compatible with a thermoplastic matrix material. Non-limiting examples of suitable polymeric film-forming materials which are compatible with a thermoplastic matrix material include the thermosetting materials, thermoplastic vinyl acetate materials and thermoplastic polyesters discussed above, as well as other thermoplastic materials discussed below and mixtures thereof.

Examples of other suitable thermoplastic film-forming materials include acrylic polymers, polyamides, polyolefins, thermoplastic polyurethanes, vinyl polymers, derivatives and mixtures thereof.

Useful acrylic polymers include polymers or copolymers of monomers such as acrylic acid; methacrylic acid; esters of these acids such as acrylates, methacrylates, ethylacrylate, propylacrylate and butylacrylate; polyglycidyl acrylates and methacrylates; acrylamides; acrylonitriles; and copolymers with unsaturated vinyl compounds such as styrene or vinyl acetate. Non-limiting examples of suitable acrylic polymers include FULATEX materials which are commercially available from H. B. Fuller Co. of St. Paul, Minnesota; RHOPLEX acrylic emulsions which are commercially available from Rohm

and Haas of Philadelphia, Pennsylvania; and CARBOSET acrylic polymers which are commercially available from B.F. Goodrich Co. of Toledo, Ohio.

Useful polyamides include the VERSAMID products which are commercially available from General Mills Chemicals, Inc. Suitable thermoplastic polyurethanes are condensation products of a polyisocyanate material and a hydroxyl-containing material such as polyol and include, for example, WITCOBOND® W-290H which is commercially available from Witco Chemical Corp. of Chicago, Illinois and RUCO 2011L which is commercially available from Ruco Polymer Corp. of Hicksville, New York.

Non-limiting examples of useful polyolefins include polypropylene and polyethylene materials such as the polypropylene emulsion RL-5440, which is commercially available from Sybron Chemicals of Birmingham, New Jersey, and Polyemulsion CHEMCOR 43C30, which is commercially available from Chemical Corp. of America.

Generally, the amount of polymeric film-forming material can be about 10 to about 90 weight percent of the first coating composition on a total solids basis, and is preferably about 60 to about 80 weight percent.

The first coating composition can additionally include one or more thermoplastic vinyl polymers, such as polyvinyl pyrrolidones, in an amount which does not detrimentally affect the compatibility of the polymeric film forming materials discussed above with the thermosetting matrix material, if present. Examples of suitable polyvinyl pyrrolidones include PVP K-15, PVP K-30, PVP K-60 and PVP K-90, each of which are commercially available from ISP Chemicals of Wayne, New Jersey. The thermoplastic vinyl polymer is preferably present in an amount of about 0.5 to about 10 weight percent of the first coating composition on a total solids basis.

The first coating composition preferably further comprises one or more glass fiber lubricants which are different from the polymeric film-forming materials discussed above. As used herein, the phrase "glass fiber lubricants

which are different from the polymeric film-forming materials" means that while the glass fiber lubricants may have film-forming properties, the glass fiber lubricant(s) selected for a particular first coating composition are chemically different from the polymeric film-forming materials included in the same coating composition.

Useful glass fiber lubricants include cationic, non-ionic or anionic lubricants and mixtures thereof. Generally, the amount of fiber lubricant can be about 1 to about 25 weight percent of the first coating composition on a total solids basis.

Non-limiting examples of such fiber lubricants include amine salts of fatty acids (which can, for example, include a fatty acid moiety having 12 to 22 carbon atoms and/or tertiary amines having alkyl groups of 1 to 22 atoms attached to the nitrogen atom), alkyl imidazoline derivatives (such as can be formed by the reaction of fatty acids with polyalkylene polyamines), acid solubilized fatty acid amides (for example, saturated or unsaturated fatty acid amides having acid groups of 4 to 24 carbon atoms such as stearic amide), condensates of a fatty acid and polyethylene imine and amide substituted polyethylene imines, such as EMERY® 6717, a partially amidated polyethylene imine commercially available from Henkel Corporation of Kankakee, Illinois.

A useful alkyl imidazoline derivative is CATION X, which is commercially available from Rhone Poulenc of Princeton, New Jersey. Other useful lubricants include RD-1135B epoxidized polyester which is commercially available from Borden Chemical of Louisville, Kentucky, CIRRASOL 185A fatty acid amide, KETJENLUBE 522 partially carboxylated polyester which is commercially available from Akzo Chemicals, Inc. Of Chicago, Illinois and PROTOLUBE HD high density polyethylene emulsion which is commercially available from Sybron Chemicals of Birmingham, New Jersey.

The first coating composition preferably comprises one or more coupling agents selected from the group consisting of organo silane coupling agents, transition metal coupling agents (such as titanium, zirconium and chromium coupling agents), amino-containing Werner coupling agents and mixtures thereof. These coupling agents typically have dual functionality. Each metal or silicon atom has attached to it one or more groups which can react or compatibilize with the glass fiber surface and/or the components of the sizing composition. As used herein, the term "compatibilize" with respect to coupling agents means that the groups are chemically attracted, but not bonded, to the glass fiber surface and/or the components of the sizing composition, for example by polar, wetting or solvation forces. Examples of hydrolyzable groups include:

$$-OR^1,\quad -O-\overset{\displaystyle O}{\overset{|}{C}}-R^2,\ -\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{|}{C}}-R^2,\ -O-N=\overset{\displaystyle R^3}{\overset{|}{C}}-R^4,\ -O-N=C—R^5, \text{ and}$$

the monohydroxy and/or cyclic C_2-C_3 residue of a 1,2- or 1,3 glycol, wherein R^1 is C_1-C_3 alkyl; R^2 is H or C_1-C_4 alkyl; R^3 and R^4 are independently selected from H, C_1-C_4 alkyl or C_6-C_8 aryl; and R^5 is C_4-C_7 alkylene. Examples of suitable compatibilizing or functional groups include epoxy, glycidoxy, mercapto, cyano, allyl, alkyl, urethano, halo, isocyanato, ureido, imidazolinyl, vinyl, acrylato, methacrylato, amino or polyamino groups.

Functional organo silane coupling agents are preferred for use in the present invention. Examples of suitable functional organo silane coupling agents include Z-6040 gamma-glycidoxypropyltrimethoxysilane (commercially available from Dow Corning), A-187 gamma-glycidoxypropyltrimethoxysilane, A-174 gamma-methacryloxypropyltrimethoxysilane and A-1100 gamma-aminopropyltriethoxysilane silane coupling agents (each of which are commercially available from OSi Specialties, Inc. of Tarrytown, New York).

The amount of coupling agent can be 1 to about 10 weight percent of the first coating composition on a total solids basis. The organo silane

coupling agent can be at least partially hydrolyzed with water prior to application to the glass fibers.

Crosslinking materials can also be included in the first coating composition. Non-limiting examples of suitable crosslinkers include melamine formaldehyde and polyamides such as the VERSAMID products which are commercially available from General Mills Chemicals, Inc. The amount of crosslinker can be about 1 to about 5 weight percent of the first coating composition on a total solids basis.

The first coating composition can include one or more emulsifying agents for emulsifying components of the first coating composition. Non-limiting examples of suitable emulsifying agents or surfactants include polyoxyalkylene block copolymers (such as PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey), ethoxylated alkyl phenols (such as IGEPAL CA-630 ethoxylated octylphenoxyethanol which is commercially available from GAF Corporation of Wayne, New Jersey), polyoxyethylene octylphenyl glycol ethers, ethylene oxide derivatives of sorbitol esters and polyoxyethylated vegetable oils (such as EMULPHOR EL-719, which is commercially available from GAF Corp.). Generally, the amount of emulsifying agent can be about 1 to about 30 weight percent of the first coating composition on a total solids basis.

The first coating composition can also include one or more aqueous dispersible or soluble plasticizers to improve flexibility. Examples of suitable non-aqueous-based plasticizers which are aqueous dispersible plasticizers include phthalates, such as di-n-butyl phthalate; trimellitates, such as trioctyl trimellitate; and adipates, such as dioctyl adipate. The amount of plasticizer is preferably less than about 5 weight percent of the first coating composition on a total solids basis.

Fungicides, bactericides and anti-foaming materials and organic and/or inorganic acids or bases in an amount sufficient to provide the aqueous first coating composition with a pH of about 2 to about 10 can also be included in the sizing composition. Water (preferably deionized) is included in the first coating composition in an amount sufficient to facilitate application of a generally uniform coating upon the strand. The weight percentage of solids of the first coating composition generally can be about 5 to about 20 weight percent.

Preferred first coating compositions for glass fiber strands for reinforcing a thermosetting matrix material are sizing compositions such as are disclosed in assignee's U.S. Patents Nos. 3,997,306 and 4,305,742, which are hereby incorporated by reference.

Another preferred first coating composition for glass fiber strands for reinforcing a thermosetting or thermoplastic matrix material includes EPON® 880 epoxy resin and RD-847-A polyester resin as the polymeric film forming materials, PVP K-30 polyvinyl pyrrolidone, EMERY® 6717 partially amidated polyethylene imine lubricant, EMULPHOR EL-719 polyoxyethylated vegetable oil, IGEPAL CA-630 ethoxylated octylphenoxyethanol, PLURONIC ™ F-108 polyoxypropylene-polyoxyethylene copolymer, SAG 10 anti-foaming material and A-174 and Z-6040 functional organo silane coupling agents.

The first coating composition can be applied in many ways, for example by contacting the filaments with a static or dynamic applicator, such as a roller or belt applicator, spraying or other means. For a discussion of suitable applicators, <u>see</u> <u>Loewenstein</u> at pages 165-172, which is hereby incorporated by reference.

The coated fibers are preferably dried at room temperature or at elevated temperatures to remove excess moisture from the fibers and cure any curable sizing or secondary coating composition components. Drying of glass fiber forming packages or cakes is discussed in detail in <u>Loewenstein</u> at

pages 219-222, which is hereby incorporated by reference. For example, the forming package can be dried in an oven at a temperature of about 104°C (220°F) to about 160°C (320°F) for about 10 to about 24 hours to produce glass fiber strands having a dried residue of the composition thereon. The temperature and time for drying the glass fibers will depend upon such variables as the percentage of solids in the first coating composition, components of the first coating composition and type of glass fiber. The first coating composition is preferably present on the fibers as a sizing in an amount ranging from about 0.5 percent to about 2.5 percent by weight after drying.

Alternatively, the first coating composition can be an impregnating or secondary coating having components such as are discussed above which are applied to at least a portion of the surface of the strands in an amount effective to coat or impregnate the portion of the strands. The secondary coating can be conventionally applied by dipping the strand in a bath containing the composition, by spraying the composition upon the strand or by contacting the strand with a static or dynamic applicator such as a roller or belt applicator, for example. The coated strand can be passed through a die to remove excess coating from the strand and/or dried as discussed above for a time sufficient to at least partially dry and cure the secondary coating.

In an alternative embodiment shown in Fig. 3, in addition to the glass fibers 320 one or more sublayers of the primary layer 312 can further comprise essentially continuous fibers or strands of materials other than glass fibers ("non-glass fibers"). Suitable non-glass fibers 331 believed to be useful in the present invention are discussed at length in the Encyclopedia of Polymer Science and Technology, Vol. 6 (1967) at pages 505-712, which are hereby incorporated by reference. As used herein, the term "fiberizable" means a material capable of being formed into a generally continuous filament, fiber, strand or yarn.

Suitable man-made fibers can be formed by a variety of polymer extrusion and fiber formation methods, such as for example drawing, melt spinning, dry spinning, wet spinning and gap spinning. Such methods are well known to those skilled in the art and further discussion thereof is not believed to be necessary in view of the present disclosure. If additional information is needed, such methods are disclosed in Encyclopedia of Polymer Science and Technology, Vol. 6 at 507-508, which is hereby incorporated by reference.

Preferably the non-glass fibers do not appreciably soften or decompose at temperatures typically encountered in thermoset molding operations and retain their tensile integrity and do not dissolve into or react with the thermosetting matrix material. It is also preferred that such non-glass fibers 331 not appreciably soften, swell or dissolve in reactive diluents such as styrene, divinyl benzene or methyl methacrylate which are often included in thermosetting polyester and vinyl ester matrix materials.

Suitable man-made fibers include synthetic polymers such as polyamides, polyesters, acrylics, polyolefins, polyurethanes, vinyl polymers, derivatives and mixtures thereof. See Encyclopedia of Polymer Science and Technology, Vol. 6 at 506, which is hereby incorporated by reference.

Non-limiting examples of useful polyamide fibers include nylon fibers such as nylon 6 (a polymer of caprolactam which has a melting point of about 223°C) and nylon 6,6 (a condensation product of adipic acid and hexamethylenediamine which has a melting point of about 264°C). Suitable nylons are commercially available from E.I. duPont de Nemours and Company of Wilmington, Delaware and BASF Corp. of Parsippany, New Jersey. Other useful polyamides include aramids such as KEVLAR™, which is commercially available from duPont.

Thermoplastic polyester fibers useful in the present invention include those composed of at least 85% by weight of an ester of a dihydric alcohol

and terephthalic acid, such as polyethylene terephthalate which has a melting point of about 265°C according to Hawley's Condensed Chemical Dictionary (12th Ed. 1993) at page 934. Examples include DACRON™ which is commercially available from duPont and FORTREL™ which is commercially available from Hoechst Celanese Corp. of Summit, New Jersey.

Other fibers which are useful in the present invention include those formed from acrylic polymers such as polyacrylonitriles having at least about 35% by weight acrylonitrile units, and preferably at least about 85% by weight, which can be copolymerized with other vinyl monomers such as vinyl acetate, vinyl chloride, styrene, vinylpyridine, acrylic esters or acrylamide. See Encyclopedia of Polymer Science and Technology, Vol. 6 at 559-561.

Useful polyolefin fibers are generally composed of at least 85% by weight of ethylene, propylene, or other olefins. See Encyclopedia of Polymer Science and Technology, Vol. 6 at 561-564.

Fibers formed from vinyl polymers which are useful in the present invention can be formed from polyvinyl chloride, polyvinylidene chloride, polytetrafluoroethylene, and polyvinyl alcohol.

Further examples of thermoplastic fiberizable materials which are useful in the present invention are fiberizable polyimides, polyether sulfones, polyphenyl sulfones; polyetherketones, polyphenylene oxides, polyphenylene sulfides and polyacetals.

Other suitable non-glass fibers for reinforcing polymeric matrix materials include natural fibers, such as cotton or jute, and inorganic fibers such as polycrystalline fibers, ceramics including silicon carbide, and carbon or graphite. It is understood that combinations of such fibers or blends or copolymers formed from any of the above materials can be used as non-glass fibers in the present invention, if desired.

Preferably, the glass fiber strands 18 comprise about 1 to about 100 weight percent of the primary layer 12 of the mat 10 on a total solids basis,

and more preferably about 50 to about 100 weight percent. If present, the non-glass fibers 331 of the primary layer 312 can comprise about 1 to about 30 weight percent of the primary layer 312 on a total solids basis, and preferably about 1 to about 10 weight percent.

Referring now to Fig. 2, the width 40 of the primary layer 12 (which corresponds generally to the overall width 42 of the mat 10 shown in Fig. 8) can range from about 0.6 to about 3 meters (about 24 to about 120 inches), and preferably ranges from about 1.2 to about 2.8 meters (about 48 to about 110 inches).

The length of the primary layer 12 can vary based upon such factors as the desired length of the product to be transported to the customer. The mat 10 is preferably formed by a generally continuous process as discussed below. Preferably, the length of the primary layer 12 ranges from about 60 to about 300 meters (about 200 to about 1000 feet), and more preferably about 180 to about 275 meters (about 600 to about 900 feet).

Referring now to Fig. 1, the thickness 44 of the primary layer 12 can range from about 2.5 to about 25 millimeters (about 0.1 to about 1 inch), and preferably ranges from about 10 to about 25 millimeters.

The surface weight of the primary layer 12 of the mat 10 can range from about 585 to about 10,350 grams per square meter (about 1.9 to about 33.8 ounces per square foot) prior to depositing the secondary layer thereon and needling the primary and secondary layers together.

Preferably, the primary layer 12 is not treated or coated with any adhesive or polymeric binder material to promote consolidation of the mat 10, although such binders can be used in accordance with the present invention. Non-limiting examples of useful polymeric binders include polyesters. Suitable polymeric binders can be in the form of a powder, fiber or emulsion, as desired. The binders are consolidated with the mat by the application of

heat and pressure, such as by passing the mat between heated calendering rolls.

An antistatic agent, for example an amine, amide or quaternary salt such as soyadimethyl ethylammonium ethosulfate, can be applied to the strands 18, 27, 43 prior to deposition upon the conveyor, if desired.

The process for forming the primary layer 12 will now be discussed. Referring now to Fig. 8, the first sublayer 17 of the primary layer 12 can be formed, for example, by positioning a plurality of forming or supply packages 46 mounted upon a creel 48 adjacent to a conveyor 50, the surface 52 of which is driven in a direction 54 by a pair of spaced drive rollers 56 which are rotated by a motor (not shown). The surface 52 of the conveyor 50 can be generally smooth or foraminous, such as a chain mesh. Useful conveyors 50 are well known to those skilled in the art and are discussed further below.

Conventional creels suitable for use in the present invention are shown in Loewenstein at page 315, which is hereby incorporated by reference. The supply packages can be wound such that the strand 18 can be withdrawn from the inside of the supply package or from the outside of the supply package (known in the art as "filling wind"). The dimensions of the supply package can vary, depending upon such variables as the diameter and type of fiber wound thereon, and are generally determined by convenience for later handling and processing. Generally, supply packages are about 15.2 to about 76.2 centimeters (about 6 to about 30 inches) in diameter and have a length of about 12.7 to about 101.6 centimeters (about 5 to about 40 inches).

The strands 18 can be aligned generally parallel to the longitudinal axis 22 of the mat 10 by tensioning each strand with a tensioning device 71, such as a weight of about 1 ounce or less, and feeding each strand 18 through a corresponding eyelet 58 mounted in a spacer board 60. The position of the eyelet 58 corresponds to the desired position of that strand 18 within the primary layer 12 of the mat 10 The aligned strands 18 are passed through a

comb 73, which can be fabricated from a low abrasion material such as ceramic or stainless steel, and then deposited onto the surface 52 of the conveyor 50. The eyelets 58 can be arranged such that a primary layer 12 having a single layer or a plurality of sublayers 319 is formed, as shown in Figs. 1 and 3, respectively. The number of eyelets 58 corresponds to the number of strands 18 to be aligned.

The diameter of each eyelet 58 is generally slightly larger than the diameter of the corresponding strand 18 passing therethrough. The eyelet 58 is preferably formed from a material which inhibits abrasion of the strand 18, such as ceramic or graphite.

Referring to Figs. 1, 2 and 8, the second sublayer 19 is deposited on the surface 21 of the first sublayer 17 by projecting one or more strands 27 across the width 40 of the first sublayer 17 of the mat 10 such that the strands are oriented generally perpendicularly to the longitudinal axis 22 of the mat 10 and the strands 18 of the first sublayer 17. The strand 27 of the second sublayer can be supplied to a strand insertion device 59 from one or more supply packages 63 mounted in a creel, in a manner such as is discussed above for supplying strand 18 to the strand feeders 74. The strand insertion device 59 projects the strand 27 across the surface 21 of the first sublayer 17 without interweaving the strand 27 within the first sublayer 17. A non-limiting example of suitable strand insertion device 59 is a projectile or shuttleless loom, such as a rapier loom or air jet loom. The first sublayer 17 is fed into the strand insertion device 59 below the region through which the strand 27 is inserted such that the strand 27 passes above the first sublayer 17 and is deposited on top of the first sublayer 17. Grippers 75 can be used at either end of the width of the strand insertion device 59 to position the strand 27 immediately prior to depositing the strand 27 onto the first sublayer 17 and sever the strand 27 from the strand supply package 63.

A non-limiting example of a suitable strand insertion device 59 is a Dornier rapier loom which is commercially available from Lindauer DORNIER GmbH of Germany. For more information on shuttleless looms, see P. Schwartz, Fabric Forming Systems, (1982) at pages 66-71, which is hereby incorporated by reference.

The distance 31 or spacing between the strands 27 of the second sublayer 19 is discussed in detail above. The thickness of the second sublayer can range from about 2.5 to about 25 millimeters. Preferably the strands 27 are deposited upon the surface 21 of the first sublayer 17 as a monolayer (shown in Fig. 1), although multiple layers can be deposited. The rate at which the strand 27 is deposited upon the surface 21 depends upon such factors as the desired spacing between the strands 27 and the rate at which the conveyor is moving.

The strands 43 of the third sublayer 23 are deposited onto the surface 25 of the second sublayer 19 and are aligned generally parallel to the longitudinal axis 22 of the mat 10 by feeding each strand 43 through a corresponding eyelet 65 mounted in the spacer board 77 and through a comb 79 in a manner similar to that discussed above for the strands 18 of the primary layer. The eyelets 65 are preferably positioned in the spacer board 77 generally vertically above the eyelets 58 such that the strands 27 of the second sublayer 19 are positioned between the strands 18 of the first sublayer 17 and the strands 43 of the third sublayer 23. The comb 79 is positioned such that the strands 43 of the third sublayer 23 are deposited upon the second sublayer 19. The strands 43 of the third sublayer 23 are maintained adjacent to the second sublayer 19 by a roller 81.

Referring now to Figs. 1 and 2, the mat 10 comprises one or more secondary layers 14 deposited upon an upper surface 16 of the primary layer 12 such that a first side 62 of the secondary layer 14 is adjacent to a second side 64 of the primary layer 12. The secondary layer 14 comprises a plurality

of randomly oriented glass fiber strands 66 which comprise generally continuous glass fiber strands 68 and/or discontinuous or chopped glass fiber strands 469.

The secondary layer 14 can comprise one or more layers of continuous glass fiber strands 68, one or more layers of chopped glass fiber strands 470 (shown in Fig. 4) and/or one or more layers of a mixture of continuous glass fiber strands 768 and chopped glass fiber strands 769 (shown in Fig. 7). The number of layers is determined by the intended end use application and desired density of the mat, although a single layer is preferred.

The secondary layer 14 can be configured in a variety of different ways. As shown in Figs. 1 and 2, a secondary layer 14 of generally continuous glass fiber strands 68 is preferred. In an alternative embodiment shown in Fig. 4, the secondary layer 414 of randomly oriented glass fiber strands 466 can be chopped glass fiber strands 469. In another alternative embodiment shown in Fig. 7, the secondary layer 714 can be a mixture of generally continuous glass fiber strands 768 and chopped glass fiber strands 769. In yet another alternative embodiment shown in Fig. 5, the secondary layer 514 comprises alternating layers of randomly oriented continuous glass fiber strands 568 and chopped glass fiber strands 569.

Referring now to Figs. 1 and 4, the randomly oriented glass fiber strands 66, 466, whether continuous or chopped, have on at least a portion of the outer surfaces 70, 470 thereof a layer 72, 472 comprising a second coating composition. The second coating composition is compatible with the polymeric matrix material (discussed in detail above). Suitable components for the second coating composition are the same as those discussed above for the first coating composition, i.e., polymeric film forming materials, thermoplastic vinyl polymers, glass fiber lubricants, emulsifiers, coupling agents, crosslinking materials, plasticizers, fungicides, bactericides, anti-

foamers and acids for adjusting the pH of the composition. The second coating composition can be applied to the randomly oriented glass fiber strands 66, 466 in a similar manner and in similar amounts to those discussed above for applying the first coating composition to the strands 18 of the primary layer 12.

The second coating composition can have the same components as those of the first coating composition in the same or different amounts. Preferably, the second coating composition has at least one different component from the first coating composition.

The components of the second coating composition are preferably those which are compatible with a thermosetting matrix material as discussed in detail above. A preferred secondary coating composition includes EPON® 828 epoxy resin and RD-847-A polyester resin as the polymeric film forming materials, PVP K-30 polyvinyl pyrrolidone, EMERY® 6717 partially amidated polyethylene imine lubricant, EMULPHOR EL-719 polyoxyethylated vegetable oil, IGEPAL CA-630 ethoxylated octylphenoxyethanol, PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer and A-174 functional organo silane coupling agent.

The dimensions of the continuous glass fiber strands 66 and chopped glass fiber strands 469 can be the same as those discussed in detail above for the strands 18 of the primary layer 12. However, the chopped fiber strands 469 preferably have a mean average length 471 ranging from about 10 to about 150 millimeters (about 0.5 to about 6 inches), and more preferably about 25 to about 100 millimeters.

Preferably, the randomly oriented, generally continuous glass fiber strands 68 comprises 100 weight percent of the secondary layer 14 on a total solids basis, as shown in Figs. 1 and 2. In the alternative embodiment shown in Fig. 7, the randomly oriented, generally continuous glass fiber strands 768 can comprise about 20 to about 100 weight percent and preferably comprises

about 50 to about 100 weight percent of the secondary layer 714 on a total solids basis, with the balance being chopped glass fiber strands 769. In the alternative embodiment shown in Fig. 4, the secondary layer 414 comprises 100 percent chopped glass fiber strands 469 on a total solids basis.

In the alternative embodiment of Fig. 3, the secondary layer 314 can comprise generally continuous and/or chopped non-glass fibers 331 such as those discussed above, preferably in an amount of about 1 to about 10 weight percent of the secondary layer 314 on a total solids basis.

Referring now to Figs. 1 and 8, in the preferred embodiment in which the glass fiber strands 66 of the secondary layer 14 are generally continuous glass fiber strands 68, the secondary layer 14 can be formed, for example, by positioning a plurality of strand feeders 74 above the conveyor 50 for depositing the secondary layer 14 upon the surface 16 of the primary layer 12.

Each strand feeder 74 is supported for reciprocating movement above the conveyor 50. The movement of each strand feeder 74 is generally transverse to the direction 54 of motion of the conveyor 50. Each strand feeder 74 receives strands 68 from a strand supply 76 and feeds the strands 68 by way of an endless belt between spaced driven pulling wheels. The pulled strands 68 are fed against a deflector plate structured to deposit the strands 68 onto the conveyor 50 as a plurality of loops 78. The strand feeders 74 are continuously traversed across the width of the conveyor such that the loops 78 are deposited across the predetermined width 80 of the secondary layer 14 to be formed.

The generally continuous glass fiber strands 68 are randomly oriented in at least two dimensions, for example by depositing the glass fiber strands 68 onto the conveyor 50 in an array of interleaved layers of generally circular, elongated elliptical and/or random loops 78, each of the loops 78 having a longitudinal axis positioned generally parallel to the longitudinal axis 22 of the

mat 10. Preferably the loops are generally elliptical. The diameter of the loops 78 can range from about 75 to about 610 millimeters (about 3 to about 24 inches).

The strand feeders 74 are controlled to form the secondary layer 14 having strands 68 oriented in a predetermined pattern and having a generally constant width and thickness which can be controlled by varying the speed at which the conveyor surface 52 or strand feeders 74 move. The speed at which the conveyor surface 52 is moved can range from about 1.5 to about 9 meters per minute (about 5 to about 30 feet per minute). The speed at which the strand feeders 74 are moved can range from about 25 to about 150 centimeters per second (about 10 to about 60 inches per second).

The number of strand feeders 74 can range from 1 to about 20, and preferably ranges from about 6 to about 20. Three strand feeders 74 are shown in Fig. 8. A non-limiting example of a strand feeder useful in the present invention is disclosed in assignee's U.S. Patent No. 4,615,717, which is hereby incorporated by reference. Preferably the strand feeder 74 includes a stationary deflector plate. Useful apparatus and processes for forming a layer of continuous strands is disclosed in assignee's U.S. Patents Nos. 3,883,333, 4,404,717, 4,615, 717, 4,692,375 and 4,995,999 and Loewenstein at pages 309-311, which are hereby incorporated by reference.

The strands can be supplied to the feeders 74 from a strand supply 76 which can be a plurality of forming or supply packages mounted upon a creel, such as are discussed above for use in forming the primary layer 12.

In an alternative embodiment, the strand supply 76 is a fiber forming apparatus which comprises a glass melting furnace or forehearth containing a supply of a fiber forming mass or molten glass and having a precious metal bushing or spinneret attached to the bottom of the forehearth. The bushing is provided with a series of orifices in the form of tips through which molten glass is drawn in the form of individual fibers or filaments at a high rate of

speed. Such fiber forming apparatus are well known to those skilled in the art and further discussion thereof is not believed to be necessary in view of the present disclosure. Suitable fiber forming apparatus are discussed in Loewenstein at pages 22-27 and 119-151, which are hereby incorporated by reference.

The glass fibers can be cooled by spraying with water (not shown) and then coated with a sizing by an applicator, such as a graphite roll applicator. After application of the sizing, the glass fibers are gathered by an alignment device which aligns each of the fibers to form one or more strands 68 in which each of the fibers is generally adjacent and coplanar (in side-by-side or generally parallel alignment). Non-limiting examples of suitable alignment devices include rotatable or stationary gathering shoes or a comb, as discussed in Loewenstein at page 173, which is hereby incorporated by reference. Preferably, the number of strands 68 ranges from 1 to about 10 strands and, more preferably, 1 to about 6 strands.

Alternatively, the fiber forming apparatus can be, for example, a forming device for non-glass fibers or strands, the methods and apparatus for which are discussed in detail above.

In the alternative embodiment shown in Fig. 4, the strands 466 of the secondary layer 414 are formed from discontinuous, chopped glass fiber strands 469. Referring to Fig. 8, there is shown in phantom a chopper 82 positioned proximate the conveyor 50 from which a supply of chopped glass fiber strands 469 is dispensed onto the surface 16 of the primary layer 12. Alternatively, the strands can be chopped at a location spaced apart from and remote to the mat forming apparatus and transported to the mat forming apparatus.

Preferably the chopper 82 dispenses about 2.8 to about 280 grams of strand per minute per linear millimeter width (about 30 to about 300 ounces per minute per linear foot width). The amount of chopped strand 469 per unit

area deposited upon the primary layer 12 is also a function of the conveyor speed.

Non-limiting examples of suitable choppers 82 include the Model 90 cutter and Model 120 inch extra wide cutters which are commercially available from Finn and Fram, Inc. of California. Useful apparatus and processes for forming a layer of chopped strands is disclosed in Loewenstein at pages 293-303, which are hereby incorporated by reference.

In the alternative embodiment shown in Fig. 6, at least a portion of the chopped glass fiber strand 669 can be opened up or filamentized, prior to forming the secondary layer 614 therefrom, by a carding machine such as are commercially available from Hollingsworth on Wheels, Inc. of Greenville, South Carolina or N. Schlumberger (USA) Inc. of Charlotte, North Carolina. Preferably the chopped strand is filamentized by passing the chopped strand through a filamentizing webber system, such as the MODEL B RANDO-WEB® processor system which is commercially available from Rando, Inc. of Macedon, New York. See "From Bale to Nonwoven Web in one Continuous Operation", a publication of Rando, Inc. (September 1990) at pages 4-5, which are hereby incorporated by reference.

The percentage of filamentized chopped strand 673 can be adjusted by adjusting the tolerances between the mating rolls of the strand opener, the rotational speed of the rolls and conveyors and by the selection of components for the coating composition and loss on ignition of the coating composition on the glass. The filamentization can also be controlled by using different coating compositions having different adhesive properties on separate portions of the glass supply. Generally the percentage of filamentized chopped strand 673 can range from about 1 to about 95 weight percent of the secondary layer 614 on a total solids basis, and preferably about 10 to about 90 weight percent.

Alternative embodiments comprising a secondary layer having a mixture of continuous glass strand 768 and chopped glass strands 769 (shown in Fig. 7) or alternating sublayers of continuous glass strand 568 and chopped glass strands 569 (shown in Fig. 5) can be produced by positioning one or more choppers 82 proximate the conveyor 50 at a predetermined distance from the strand feeders 74 in the direction 54 such that chopped strands ejected from the chopper 82 are deposited upon the upper surface 16 of the primary layer 12 of generally continuous strands 18.

The dimensions and physical characteristics of the secondary layer 14 will now be discussed. Referring to Fig. 2, the width 80 of the secondary layer 14 (which can be greater than or correspond generally to the overall width 42 of the mat 10) can range from about 0.6 to about 3 meters (about 24 to about 120 inches), and preferably ranges from about 1.2 to about 2.8 meters (about 48 to about 110 inches). The length of the secondary layer 14 corresponds generally to the length of the primary layer 12.

The thickness 84 of the secondary layer 14 can range from about 5 to about 305 millimeters (about 0.25 to about 12 inches) prior to needling. The surface weight of the secondary layer 14 of the mat 10 can range from about 715 to about 1150 grams per square meter prior to needling (about 2.3 to about 4 ounces per square foot).

Referring now to Fig. 3, there is shown a mat 310 comprising alternating primary layers 312 and secondary layers 314. Such a mat 310 can be formed by forming a mat 10 having a primary layer 12 and secondary layer 14 such as discussed above and stacking a plurality of mats 10 prior to needling, for example.

The number of primary layers 312 and secondary layers 314 can vary as desired, and can be a function of cost and the desired overall mat thickness. The number of layers 312, 314 can range from 1 to about 5. Three primary layers 312 and three secondary layers 314 are shown in Fig. 3.

Alternatively, the mat 310 can comprise a different number of primary layers 312 than secondary layers 314.

As shown in Fig. 3, in an alternative embodiment the mat 310 can include a film of non-glass material or a fabric 333 of glass fibers and/or non-glass fibers (as defined above), such as an engineered knit, woven fabrics or woven roving, within or between the primary layers 312 and secondary layers 314.

Referring now to Fig. 8, the strands 18 of the primary layer 12 are preferably entangled with the strands 66 of the secondary layer 14 by needling the strands 18 of the primary layer 12 with the strands 66 of the secondary layer 14 together. Alternatively, the strands 18 of the primary layer 12 can be hydro-entangled with the strands 66 of the secondary layer 14.

As shown in Fig. 8, the needling can be accomplished by passing the mat 10 through a needler 86 between generally known spaced needling boards 88, such as are disclosed in assignee's U.S. Patent No. 4,277,531, which is hereby incorporated by reference.

A plurality of spaced needles 90 are used to entangle or intertwine the strands 18, 66 of the mat 10 to impart mechanical strength and integrity to the mat 10. The needles 90 are constructed and arranged with a barb which entangles the strands 18, 66 contained in the mat 10 as the needles 90 pass through the mat 10 forming aperture 92 (shown for example if Figs. 1 and 2) on the downward stroke of the vertical reciprocation of the needles 90 and preferably release the fibers 18, 66 contained within the mat 10 during the upward stroke of the reciprocating needler. Alternatively, needles with reverse barbs can be used to form the mat of the present invention. As used herein, the term "horizontal(ly)" means that the direction of movement is generally parallel with respect to ground 94. As used herein, the term "vertical(ly)", "downwardly" and "upwardly" refer to direction of movement which is generally perpendicular with respect to ground 94.

During vertical upward movement 96, the needles 90 are passed through a plurality of generally cylindrical orifices in a metal stripper plate (not shown for clarity in the drawings) which rests upon the mat 10 during its passage throughout the needler 86. The strands 18 are thus pulled from the surface of the barb as the mat 10 proceeds in horizontal direction 54 after a stroke of the needle 90 in a downward and upward direction. The mat 10 passes over a metal bed plate 98 having a plurality of generally cylindrical orifices therethrough aligned with the orifices of the stripper plate through which the needles 90 pass on the downward stroke of the needleboard 88.

The needleboard 88 can be reciprocated such that a full stroke (downward and upward motion) occurs in a period of about 100 to about 1000 strokes per minute and upon completion of each reciprocation rollers 100 are provided in association with the needler 86 to move the mat 10 in the generally horizontal direction 54 in preparation for the successive downward stroke of the needleboard 88.

A non-limiting example of a suitable needling machine is Model NL 9 which is commercially available from Textilmaschinenfabrik Dr. Ernest Fehrer AG of Germany.

The length of the needle 90, the depth of the penetration of the needle 90 through the mat 10 during its passage through the needler 86 and the extent to which the fibers 18, 66 entangled in the barb of the needle 90 are moved in a generally vertical upward direction 96 through the mat 10 during the upward stroke of the needler 86 determine the extent to which impact strength can be imparted to the composite 913 (shown in Fig. 9) incorporating the mat 10 as reinforcement.

Preferably, the gauge of the needle 90 ranges from about 32 to about 19 gauge, with a combination of 25 and 32 gauge needles being preferred. The punch density is preferably about 10 to about 100 punches per square centimeter.

The punching depth or degree of penetration of the needles into the orifices of the bed plate 98 preferably ranges from about 7.5 to about 20 millimeters (about 0.3 to about 0.8 inches). In a typical needling process, the mat 10 entering the needler 86 can have an overall average thickness of about 9 to about 307 millimeters. After passage throughout the needler 86, the mat 10 can have a compressed overall average thickness 102 of about 5 to about 20 millimeters (about 0.2 to about 0.8 inches). The needling process is described in further detail in assignee's U.S. Patent No. 4,335,176, which is hereby incorporated by reference.

The surface weight of the mat 10 after needling can range from about 1300 to about 11,500 grams per square meter (about 4.25 to about 37.6 ounces per square foot), and preferably about 1300 to about 8000 grams per square meter. The overall width 42 of the mat 10 can range from about 0.6 to about 3 meters (about 24 to about 120 inches), and preferably ranges from about 1.2 to about 2.8 meters (about 48 to about 110 inches).

An advantage of such a mat 10 is that it can be readily handled after formation and packaged in a convenient form for transportation to a customer. For example, as shown in Fig. 8, the mat 10 can be rolled to form a roll 104 or festooned or severed into predetermined lengths and packaged in a conventional container 106 of suitable dimensions for shipment to the customer.

Referring now to Fig. 9, the mat 910 can be used to reinforce a polymeric matrix material 911 to form a polymeric composite 913, by any method known in the art, for example by compression molding, vacuum molding, open lay-up molding using resin and glass fiber spray-up equipment, preforms for press molding, sheet molding and dough molding, pultrusion, filament winding and panel formation processes. The preferred method for forming a composite 913 of the present invention is by vacuum molding. A preferred vacuum molding process is disclosed in U.S. Patents Nos.

4,902,215; 5,052,906; 5,316,462; and 5,439,635, which are hereby incorporated by reference. The mats of the present invention provide cost savings and decreased fabrication time in such vacuum molding processes since a single mat can be used for reinforcement rather than multiple mats. Also, the mats of the present invention provide good directionalized and cross-strength to composites for applications such as columns, pilings and poles.

The polymeric matrix material 911 is preferably a thermosetting matrix material, although the present mat 910 is also useful for reinforcing thermoplastic matrix materials.

Thermosetting matrix materials 911 useful in the present invention include thermosetting polyesters, vinyl esters, epoxides, phenolics, aminoplasts, thermosetting polyurethanes, derivatives and mixtures thereof. Preferably the thermosetting matrix material is a polyester or vinyl ester.

Suitable thermosetting polyesters include the AROPOL products which are commercially available from Ashland Chemical Inc. of Columbus, Ohio. Examples of useful vinyl esters include DERAKANE® products such as DERAKANE® 470-45, which are commercially available from Dow Chemical USA of Midland, Michigan.

Useful epoxides are discussed in detail above. Examples of suitable commercially available epoxides are EPON® 826 and 828 epoxy resins, which are epoxy functional polyglycidyl ethers of bisphenol A prepared from bisphenol-A and epichlorohydrin and are commercially available from Shell Chemical.

A non-limiting example of a useful phenolic is phenol-formaldehyde. and RESIMENE 841 melamine formaldehyde from Monsanto. An example of a suitable thermosetting polyurethane is STR-400, which is commercially available from Bayer.

Non-limiting examples of suitable polymeric thermoplastic matrix materials include polyolefins, polyamides, thermoplastic polyurethanes, thermoplastic polyesters, acrylic polymers, vinyl polymers, derivatives and mixtures thereof.

Non-limiting examples of useful polyolefins include polyethylene, extended-chain polyethylene, polypropylene, polybutene, polyisoprene, and polypentene, polymethyl pentene, polytetrafluoroethylene and neoprene.

Useful polyamides include nylons such as nylon 6 (a polymer of caprolactam), nylon 12 (which can be made from butadiene), nylon 66 (a condensation product of adipic acid and hexamethylenediamine), nylon 10 and nylon 12 such as are commercially available from DuPont. Other examples of useful polyamides include polyhexamethylene adipamide and aramids such as Kevlar™, which is commercially available from duPont.

Suitable thermoplastic polyurethanes are condensation products of a polyisocyanate material and a hydroxyl-containing material such as polyol and include, for example, Estane and Texin polyurethanes which are commercially available from B.F. Goodrich of Toledo, Ohio and Bayer, respectively.

Thermoplastic polyesters useful in the present invention include polyethylene terephthalate and polybutylene terephthalate. Acrylic polymers useful in the present invention include polyacrylates, polyacrylamides and polyacrylonitriles such as nitrile rubber.

Useful vinyl polymers include polyvinyl chloride, polyvinylidene chloride (saran), polyvinyl fluoride, polyvinylidene fluoride, ethylene vinyl acetate copolymers, such as Elvax which is commercially available from duPont, and polystyrenes.

Thermoplastic elastomeric materials useful as matrix materials in the present invention include styrene-butadiene rubbers, styrene-acrylontrile (SAN) copolymers such as Lustran, which is commercially available from

Monsanto of St. Louis, Missouri, styrene-butadiene-styrene (SBS) copolymers and acrylonitrile-butadiene-styrene (ABS) copolymers, such as Cycolac or Blendex, which are commercially available from GE Plastics of Pittsfield, Massachusetts.

Further examples of useful thermoplastic materials include polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polyvinyl chlorides and polycarbonates. Also included as suitable thermoplastic materials are any of the above thermoplastics which are modified by an unsaturated monomer.

Other components which can be included with the polymeric matrix material 911 and reinforcing mat 910 in the composite 913 are, for example, colorants or pigments, lubricants or process aids, ultraviolet light (UV) stabilizers, antioxidants, other fillers, and extenders.

The mat 910 and polymeric matrix material(s) 911 can be formed into a composite 913 by a variety of methods which are dependent upon such factors as the type of polymeric matrix material 911 used.

Thermosetting matrix materials can be cured by application of heat. The temperature and curing time for the thermosetting matrix material depends upon such factors as the type of thermosetting matrix material used, other additives in the matrix system and thickness of the composite, to name a few.

Thermoplastic composites can be formed by first forming a laminate of the mat 910 and thermoplastic matrix material and then compression molding or stamping the laminate. To form the laminate the thermoplastic matrix material can be impregnated into the mat 910 and then the impregnated mat can be heated in a oven, such as a conventional continuous oven well known to those skilled in the art, at a temperature of about 190°C to about 240°C for about 7 minutes. The laminate can be transferred to a mold and heated under pressure to a temperature which can vary based upon the resin

selected. For example, for polypropylene, the molding temperature can be about 65°C. The pressure for forming such a laminate can be about 14 MPascals. One skilled in the art would understand that the laminating and molding temperatures and pressure can vary based upon such factors as the dimensions and structure of the composite to be formed and the thermoplastic matrix material.

A method according to the present invention for making a mat adapted to reinforce a polymeric matrix material will now be described generally.

With reference to Fig. 8, the method generally comprises the initial step of positioning a plurality of generally parallel, essentially continuous glass fiber strands 18 generally perpendicularly to a longitudinal axis 22 of the mat 10 to form a first sublayer 17 of a primary layer 12. A plurality of generally parallel, essentially continuous glass fiber strands 27 is positioned on the surface 21 of the first sublayer 17 and oriented generally perpendicularly to the longitudinal axis 22 of the mat 10 and the strands 18 of the first sublayer 17 to form a second sublayer 27. A plurality of generally parallel, essentially continuous glass fiber strands 43 is positioned upon a surface 25 of the second sublayer 27 generally perpendicularly to the longitudinal axis 22 of the mat 10 to form a third sublayer 23.

In a preferred embodiment, a plurality of essentially continuous glass fiber strands 66 is dispersed upon the third sublayer 23 of the primary layer 12 to form a secondary layer 14, such that the glass fiber strands 66 of the secondary layer 14 are randomly oriented as discussed above. The strands 66 are preferably dispersed by one or more strand feeders 74 in a manner such as is discussed in detail above. The strands 66 have on at least a portion thereof a second coating composition which is compatible with the thermosetting matrix material, discussed in detail above.

Alternatively or additionally, a plurality of chopped glass fiber strands 469 is dispersed upon the third sublayer 23 of the primary layer 412, the

strands 469 having a mean average length such as is discussed above. The strands 469 can be dispersed onto the primary layer 412 from a chopper 82 in a manner such as is discussed in detail above.

The glass fiber strands 18, 27, 43 of the primary layer 12 are entangled with the glass fiber strands 66 of the secondary layer 14 by needling the strands 18, 27, 43, 66 of the layers 12, 14 together to form the mat 10. Suitable needlers and the methods for needling are discussed in detail above.

A method according to the present invention for reinforcing a polymeric matrix material to form a reinforced composite will now be described generally. The method comprises the initial steps of forming a first sublayer 17, a second sublayer 27 and a third sublayer 23, as discussed above.

In a preferred embodiment, a plurality of essentially continuous and/or chopped glass fiber strands 66 is dispersed upon the primary layer 12 to form a secondary layer 14, such that the glass fiber strands 66 of the secondary layer 14 are randomly oriented as discussed above. Methods and apparatus for forming and needling the mat 10 are discussed in detail above.

In a preferred embodiment, at least a portion of the mat 10 is coated and impregnated with the thermosetting matrix material 911. The thermosetting matrix material 911 is at least partially cured to form the reinforced composite 913, preferably by the application of heat or a curing agent such as discussed above.

In an alternative embodiment, at least a portion of the mat 10 is coated and impregnated with a thermoplastic matrix material. The thermoplastic matrix material is heated to a temperature sufficient to permeate the mat and is cooled to ambient temperature to provide a reinforced thermoplastic composite, as discussed above.

The mats of the present invention have sufficient structural integrity to resist damage during transportation and handling and are useful in a wide variety of molding processes. The mats of the present invention exhibit good

formability and structural integrity which facilitates handling of the mat and enables the fabricator to decrease mold cycle times. The ability to mold with a single ply can reduce cost and decrease fabrication time.

Other advantages of the mats of the present invention include good flexibility and high density to provide good load bearing capabilities, high shear strength, compressive strength and interlaminar shear strength, good cross directional uniformity, low washing or squeeze out during mat compaction during molding, low delamination and springback of the mat during composite formation, good flexibility, processing and sheet loft performance, high reinforcement weight capability, good flow and knitline properties, good surface and blister characteristics.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications which are within the spirit and scope of the invention, as defined by the appended claims.

THEREFORE, WE CLAIM:

1. A mat adapted to reinforce a polymeric matrix material, the mat comprising:

(a) a non-woven primary layer comprising (i) a first sublayer of a plurality of generally parallel, essentially continuous glass fiber strands oriented generally parallel to a longitudinal axis of the mat; (ii) a second sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the first sublayer and being oriented generally perpendicularly to the longitudinal axis of the mat; (iii) a third sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat; and

(b) a secondary layer positioned adjacent to a surface of the primary layer, the secondary layer comprising a plurality of randomly oriented, generally continuous glass fiber strands, wherein the strands of the primary layer are entangled with the strands of the secondary layer by needling together at least a portion of the strands of the primary layer and the strands of the secondary layer to form a mat.

2. The mat according to claim 1, wherein the glass fiber strands of the primary layer have on at least a portion of the outer surfaces thereof a first coating composition which is compatible with a thermosetting matrix material, the first coating composition comprising a polymeric film-forming material which is selected from the group consisting of thermosetting materials, vinyl acetate materials and thermoplastic polyester materials.

3. The mat according to claim 1, wherein the glass fiber strands of the primary layer have on at least a portion of the outer surfaces thereof a first coating composition which is compatible with a thermoplastic matrix material.

4. The mat according to claim 1, wherein an average distance between a pair of adjacent strands of the primary layer ranges from about 0.1 to about 20 millimeters.

5. The mat according to claim 1, wherein the primary layer comprises about 20 to about 90 weight percent of the mat on a total solids basis.

6. The mat according to claim 1, wherein the first sublayer (i) of the primary layer of the mat comprises about 10 to about 50 weight percent of the primary layer of the mat on a total solids basis.

7. The mat according to claim 1, wherein the second sublayer (ii) of the primary layer of the mat comprises about 10 to about 50 weight percent of the primary layer of the mat on a total solids basis.

8. The mat according to claim 1, wherein the third sublayer (iii) of the primary layer of the mat comprises about 10 to about 50 weight percent of the primary layer of the mat on a total solids basis.

9. The mat according to claim 1, wherein the glass fiber strands of the secondary layer have on at least a portion of the outer surfaces thereof a second coating composition which is compatible with the thermosetting matrix material, the second coating composition comprising a polymeric film-forming

material which is selected from the group consisting of thermosetting materials, vinyl acetate materials and thermoplastic polyester materials.

10. The mat according to claim 1, wherein the glass fiber strands of the secondary layer have on at least a portion of the outer surfaces thereof a second coating composition which is compatible with a thermoplastic matrix material.

11. The mat according to claim 1, wherein the plurality of randomly oriented, generally continuous glass fiber strands of the secondary layer comprises about 50 to about 100 weight percent of the secondary layer on a total solids basis.

12. The mat according to claim 1, wherein the primary layer and secondary layer are needled together at a punch density ranging from about 10 to about 100 punches per square centimeter.

13. The mat according to claim 1, wherein the surface weight of the mat ranges from about 1300 to about 11,500 grams per square meter

14. The mat according to claim 1, wherein the mat further comprises a plurality of primary layers.

15. The mat according to claim 1, wherein the mat further comprises a plurality of secondary layers.

16. The mat according to claim 1, wherein the secondary layer further comprises a plurality of randomly oriented glass fibers having a mean average length ranging from about 10 to about 150 millimeters.

17. The mat according to claim 14, wherein at least a portion of the glass fibers of the secondary layer are present as discrete monofilaments.

18. The mat according to claim 1, wherein the mat further comprises a plurality of non-glass fibers.

19. The mat according to claim 1, further comprising a woven fabric layer comprising a plurality of glass fibers.

20. A mat adapted to reinforce a polymeric matrix material, the mat comprising:

(a) a non-woven primary layer comprising (i) a first sublayer of a plurality of generally parallel, essentially continuous glass fiber strands oriented generally parallel to a longitudinal axis of the mat; (ii) a second sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the first sublayer and being oriented generally perpendicularly to the longitudinal axis of the mat; (iii) a third sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat; and

(b) a secondary layer positioned adjacent to a surface of the primary layer, the secondary layer comprising a plurality of randomly oriented glass fibers having a mean average length ranging from about 10 to about 150 millimeters, wherein the strands of the primary layer are entangled with the strands of the secondary layer by needling together at least a portion of the strands of the primary layer and the fibers of the secondary layer to form a mat.

21. The mat according to claim 20, wherein at least at least a portion of the glass fibers of the secondary layer are present as discrete monofilaments.

22. A reinforced polymeric composite comprising:

(a) a polymeric matrix material; and

(b) a reinforcing mat comprising:

(1) a non-woven primary layer comprising (i) a first sublayer of a plurality of generally parallel, essentially continuous glass fiber strands oriented generally parallel to a longitudinal axis of the mat; (ii) a second sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the first sublayer and being oriented generally perpendicularly to the longitudinal axis of the mat; (iii) a third sublayer of a plurality of generally parallel, essentially continuous glass fiber strands positioned upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat; and

(2) a secondary layer positioned adjacent to a surface of the primary layer, the secondary layer comprising a plurality of randomly oriented, generally continuous glass fiber strands, wherein the strands of the primary layer are entangled with the strands of the secondary layer by needling together at least a portion of the strands of the primary layer and the strands of the secondary layer to form a mat for reinforcing the polymeric matrix material.

23. The composite according to claim 22, wherein the polymeric matrix material is a thermosetting film-forming material selected from the group consisting of thermosetting polyesters, vinyl esters, epoxides, phenolics, aminoplasts, thermosetting polyurethanes, derivatives and mixtures thereof.

24. The composite according to claim 22, wherein the polymeric matrix material is a thermoplastic film-forming material selected from the group consisting of polyolefins, polyamides, thermoplastic polyurethanes, thermoplastic polyesters, acrylic polymers, vinyl polymers, derivatives and mixtures thereof.

25. A method for making a mat adapted to reinforce a polymeric matrix material, the method comprising the steps of:

(a) positioning a plurality of generally parallel, essentially continuous glass fiber strands generally parallel to a longitudinal axis of the mat to form a first sublayer of a primary layer;

(b) positioning a plurality of generally parallel, essentially continuous glass fiber strands upon a surface of the first sublayer and being oriented generally perpendicularly to the longitudinal axis of the mat to form a second sublayer of the primary layer;

(c) positioning a plurality of generally parallel, essentially continuous glass fiber strands upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat to form a third sublayer of the primary layer;

(d) dispersing a plurality of essentially continuous glass fiber strands upon a surface of the primary layer to form a secondary layer, such that the glass fiber strands of the secondary layer are randomly oriented; and

(e) entangling the glass fiber strands of the primary layer with the glass fiber strands of the secondary layer by needling at least a portion of the strands of the primary layer and the strands of the secondary layer together to form a mat.

26. A method for reinforcing a polymeric matrix material to form a reinforced composite, the method comprising the steps of:

(a) positioning a plurality of generally parallel, essentially continuous glass fiber strands generally parallel to a longitudinal axis of the mat to form a first sublayer of a primary layer;

(b) positioning a plurality of generally parallel, essentially continuous glass fiber strands upon a surface of the first sublayer and being oriented generally perpendicularly to the longitudinal axis of the mat to form a second sublayer of the primary layer;

(c) positioning a plurality of generally parallel, essentially continuous glass fiber strands upon a surface of the second sublayer and being oriented generally parallel to a longitudinal axis of the mat to form a third sublayer of the primary layer;

(b) dispersing a plurality of essentially continuous glass fiber strands upon a surface of the primary layer to form a secondary layer, such that the glass fiber strands of the secondary layer are randomly oriented;

(c) entangling the glass fiber strands of the primary layer with the glass fiber strands of the secondary layer by needling at least a portion of the strands of the primary layer and the strands of the secondary layer together to form a mat;

(d) coating and impregnating at least a portion of the mat with the polymeric matrix material; and

(e) at least partially curing the polymeric matrix material to form a reinforced composite.

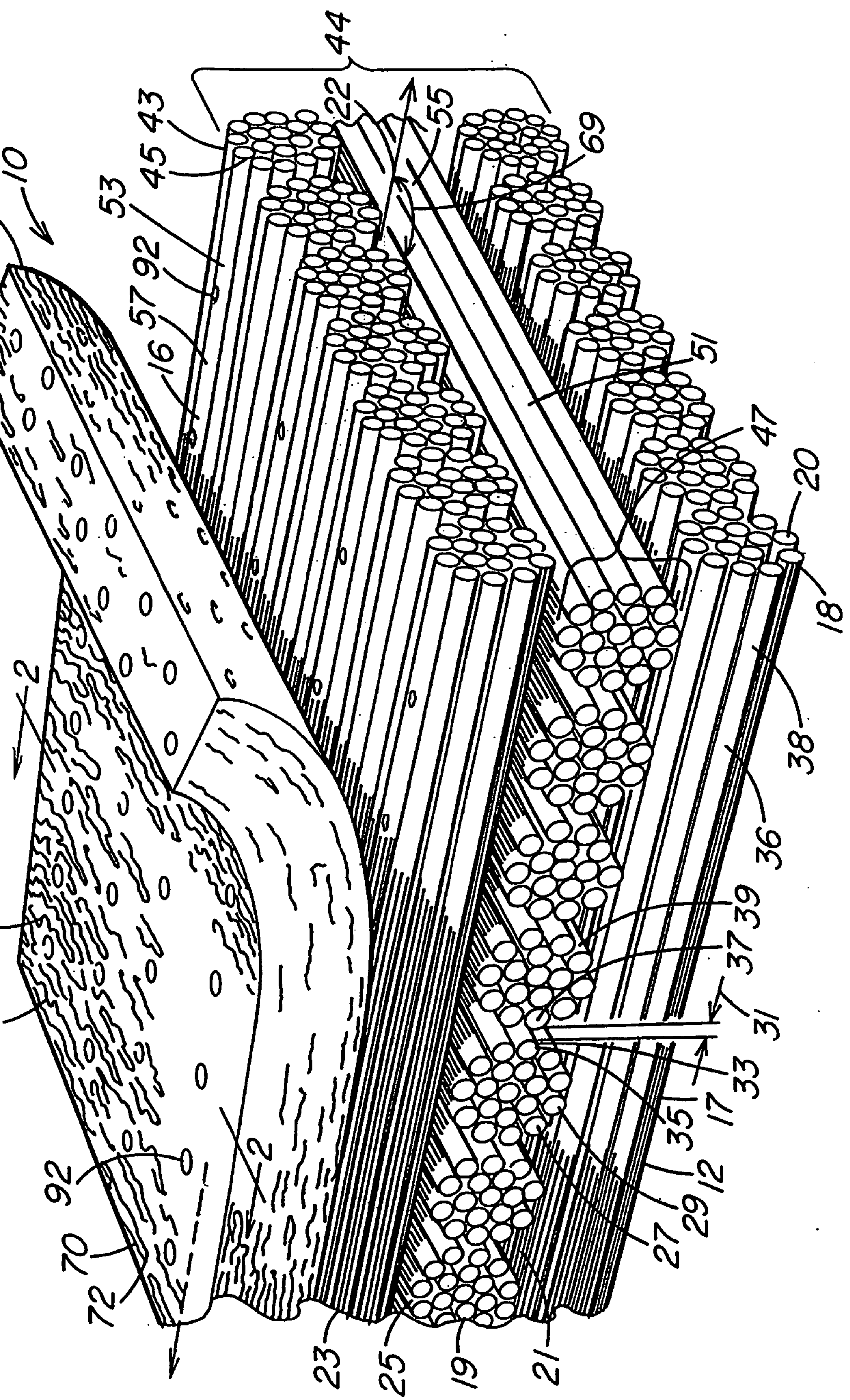
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FIG. 1

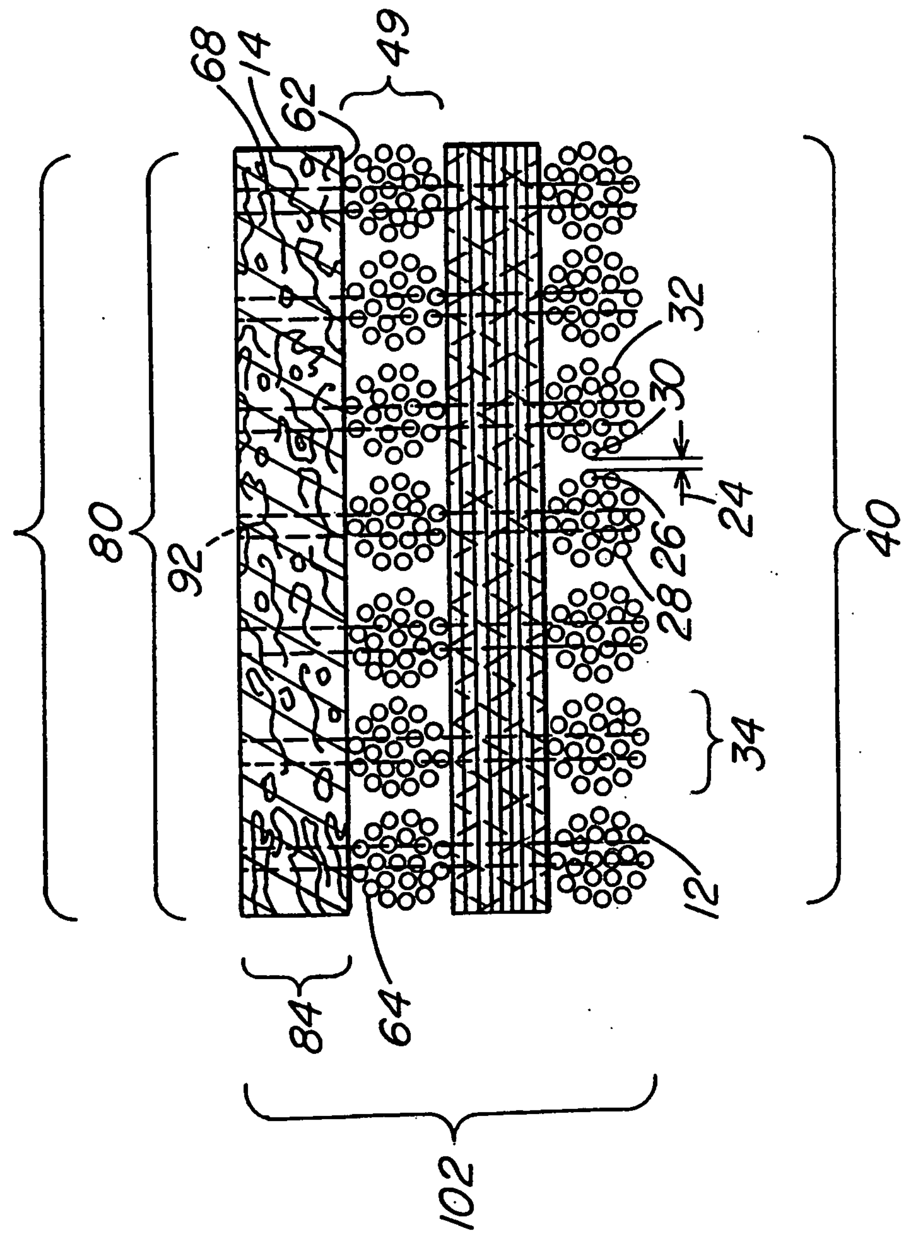

FIG. 2

FIG. 3

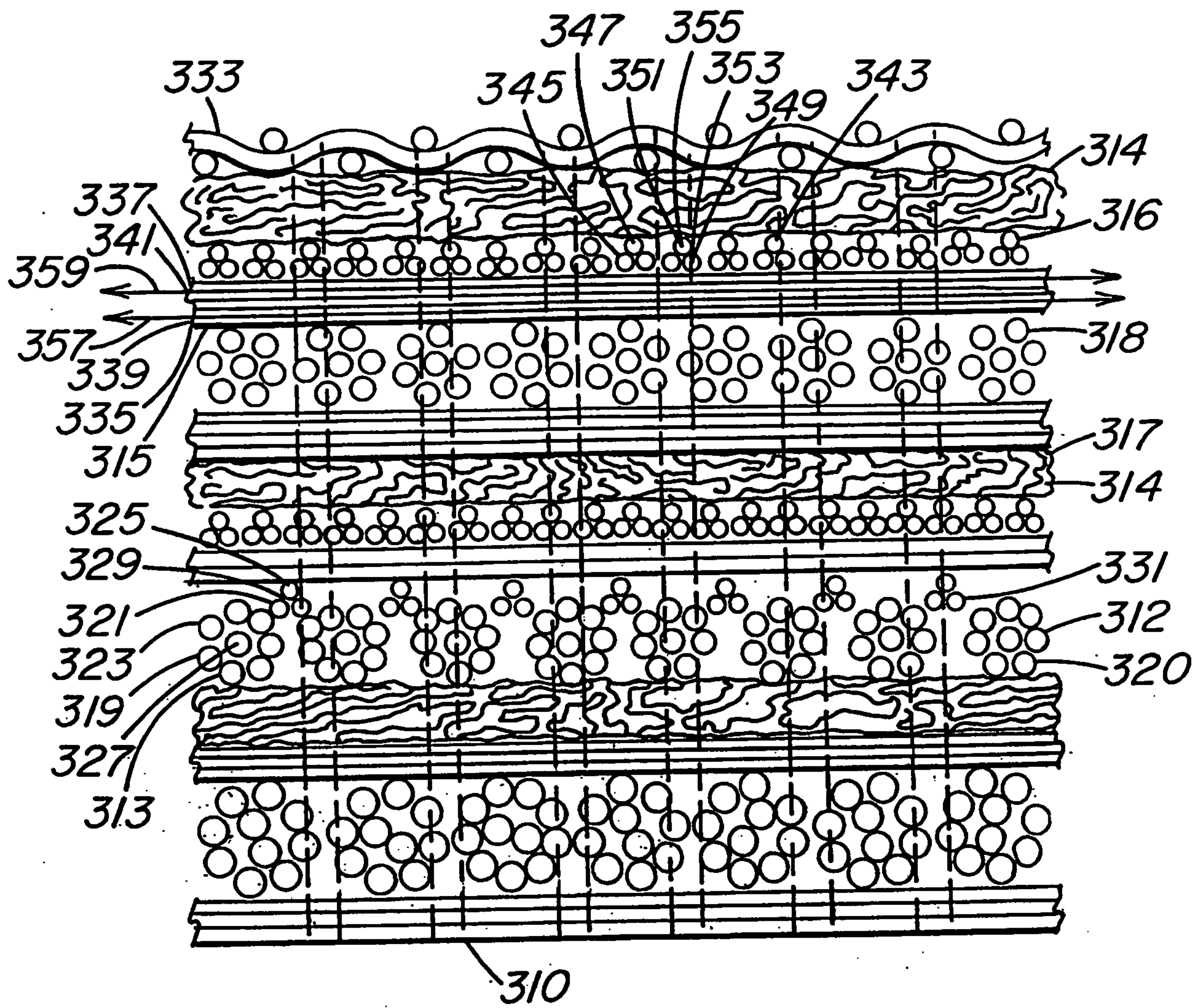
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FIG. 4

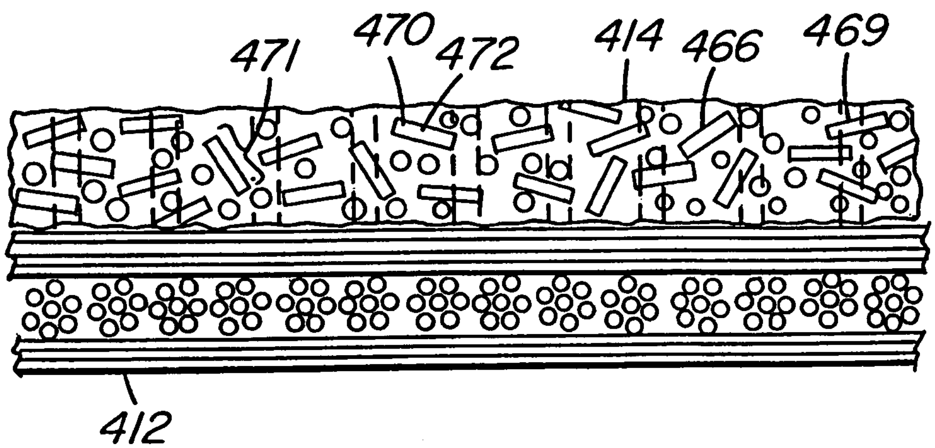


FIG. 5

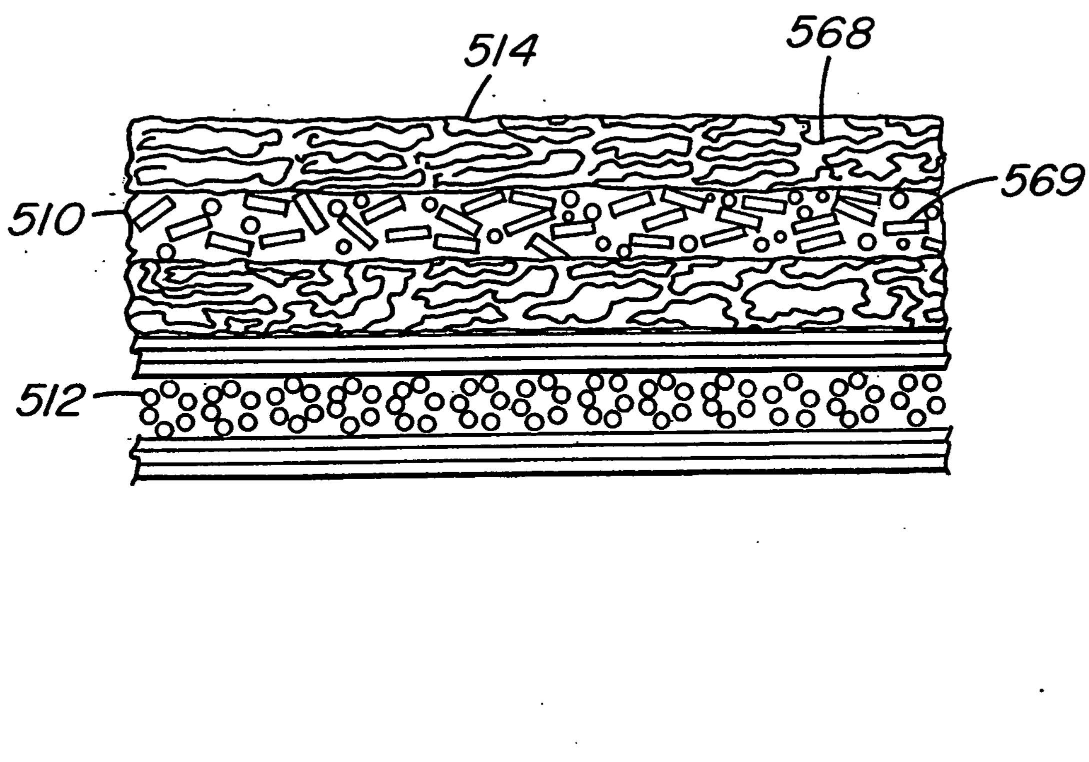
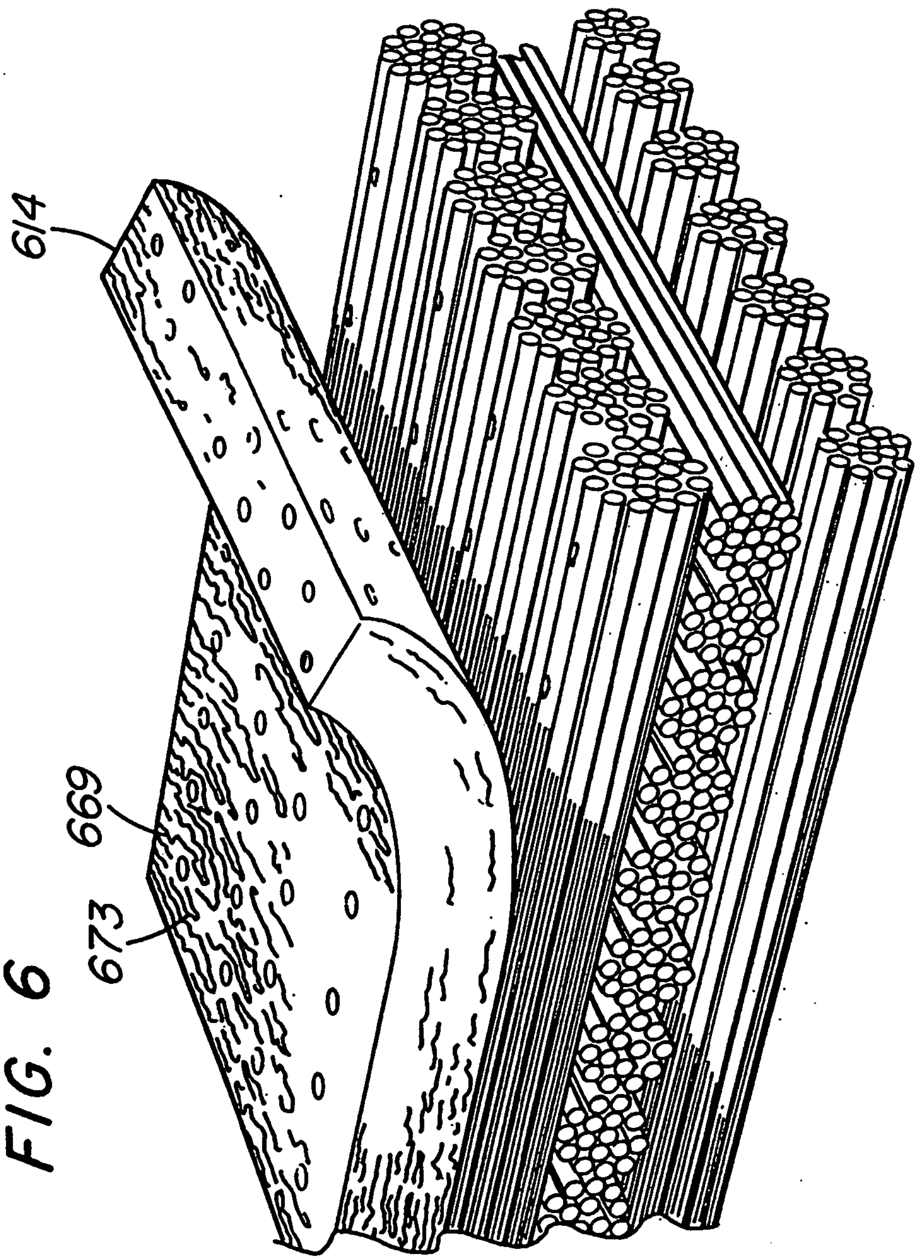


FIG. 6



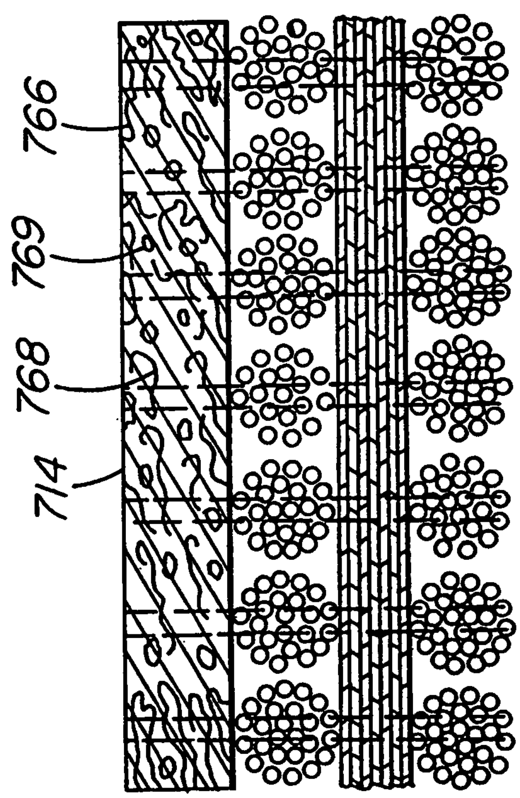


FIG. 7

FIG. 8

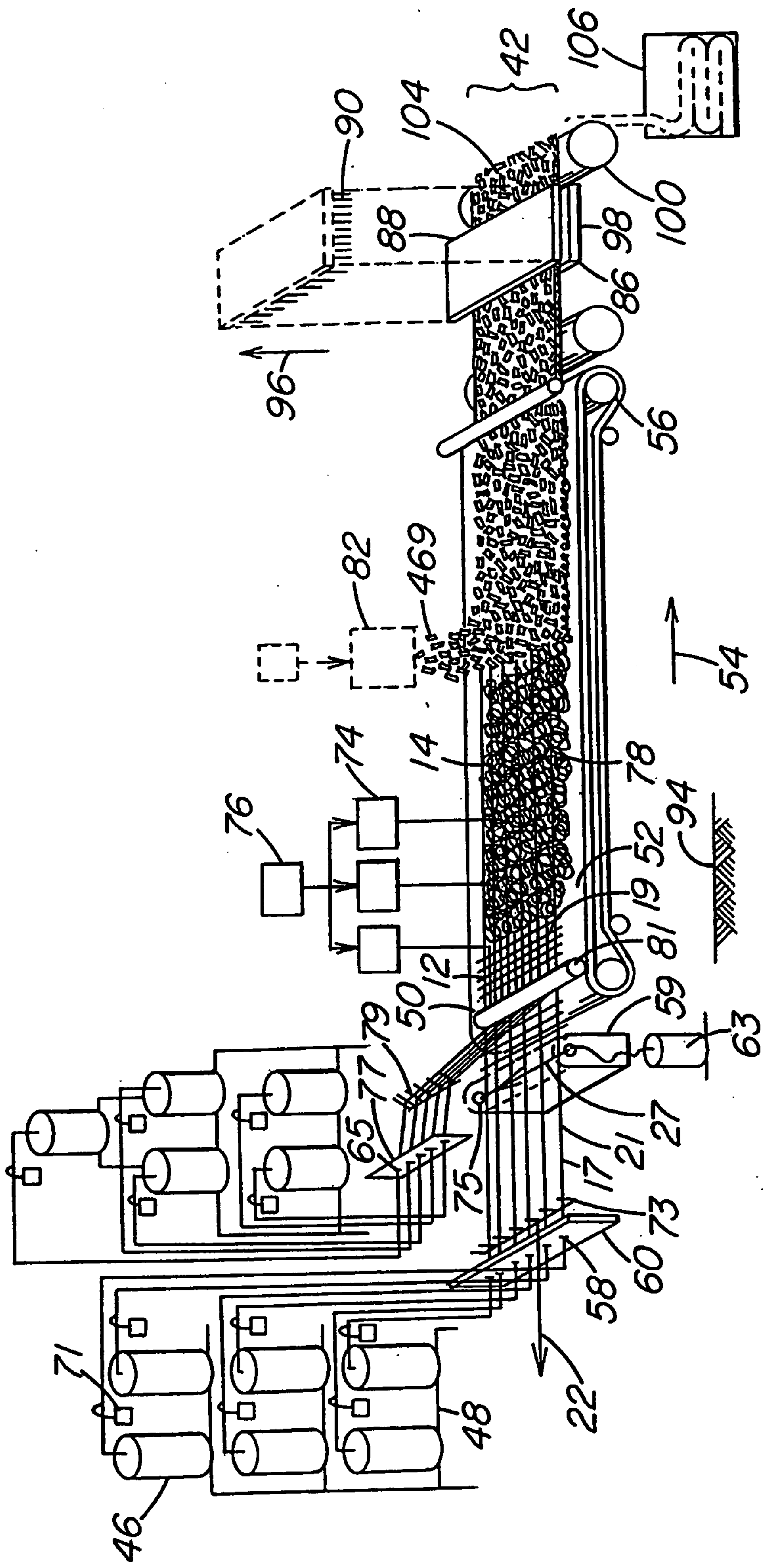

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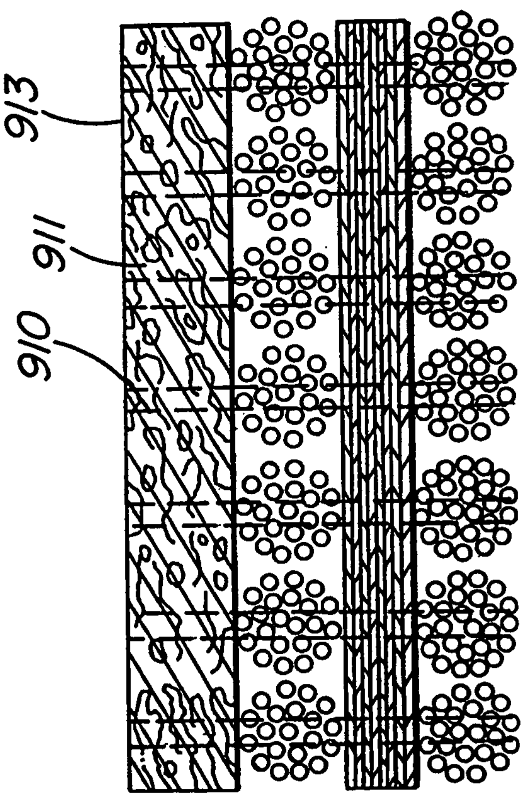
FIG. 9



A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C67/00 C03C25/02 B32B5/06 D04H13/00 B32B5/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C C03C B32B D04H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 221 336 A (PPG INDUSTRIES INC) 13 May 1987 see the whole document ---	1-26
A	FR 2 547 238 A (BASF AG) 14 December 1984 see page 2, line 15 - page 4, line 35 ---	1-26
A	EP 0 646 454 A (SYMALIT AG) 5 April 1995 see claims 1,2,5 ---	1-26
A	US 3 614 936 A (PHILIPPS THOMAS E) 26 October 1971 cited in the application see column 1, line 66 - line 68; claims 8,9; figure 3 --- -/--	1-26

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
27 August 1998	07/09/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Barathe, R

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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